

BEST AVAILABLE COPY
864/51.439

PCT/EP2004/031439



**Europäisches
Patentamt**

**European
Patent Office**

**Office européen
des brevets**

REC'D 01 NOV 2004

WIPO

PCT

Bescheinigung

Certificate

Attestation

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03102321.1

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Europäisches
Patentamt

POI/EP 200 4 / 0 0 1 4 0 0
European
Patent Office
Office européen
des brevets

Anmeldung Nr:
Application no.: 03102321.1
Demande no:

Anmeldetag:
Date of filing: 28.07.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

KRATON Polymers Research B.V.
Badhuisweg 3
1031 CM Amsterdam
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Method for partially and selectively hydrogenating polymers made of conjugated
dienes

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C08F/

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

METHOD FOR PARTIALLY AND SELECTIVELY HYDROGENATING POLYMERS MADE OF CONJUGATED DIENES

Field of the Invention

The invention relates to a method for partially and selectively hydrogenating a polymer made of at least a conjugated diene monomer comprising a hydrogenation step on a solution of the polymer.

Background of the Invention

Polymers based on conjugated dienes and copolymers based on said conjugated dienes and vinyl aromatic monomers are known elastomers. A selected group thereof is the group composed of thermoplastic elastomers, i.e. block copolymers comprising elastomeric polymer blocks and separate polymer blocks providing physical cross-links. It is also known that the properties of these polymers (in terms of stability and aging and the like) may be improved by hydrogenating the residual olefinic unsaturation.

The first hydrogenation processes appeared to hydrogenate all residual unsaturation and indeed even all aromatic unsaturation in case of aromatic copolymers. Since this had a substantial impact on the properties of the polymers, so-called selective hydrogenation catalysts were developed. These catalysts only hydrogenate the olefinic unsaturated carbon-carbon bonds. Such hydrogenation processes are nearly always based on nickel-, cobalt-, or titanium-containing catalysts.

Hydrogenating poly(1,4-butadiene) would result in a fully saturated polyolefin without elastomeric properties. It has therefore been recognized that elastomers should have a polymer backbone containing a minimum of about 20 % vinyl groups (1,2-olefinic bonds), which are composed of conjugated

dienes that are polymerized in a 1,2-fashion, as well as recurring groups made by polymerization in a 1,4-fashion.

For certain applications, the use of selective, partially hydrogenated elastomers would be desirable. For instance, in
5 WO 02/44281 bituminous compositions are disclosed with reduced gelation tendency. Ideally, elastomers should have a content of conjugated dienes polymerized in a 1,2-fashion (so-called vinyl content) of 20 to 65% before hydrogenation, and of less than 5% after hydrogenation, whereas the content of conjugated
10 dienes polymerized in a 1,4-fashion of 80 to 30% before hydrogenation is not reduced to less than 30% after hydrogenation. Preferably, an elastomer having a vinyl content of 30 to 60% is hydrogenated to an extent wherein the vinyl content is reduced to less than 3%, whereas the 1,4-content is
15 still maintained at a level of at least 30%. In the context of the present invention, the expressions "selective" and "partial" hence refer to the hydrogenation of only certain of the olefinic unsaturated carbon-carbon bonds.

Inexpensive catalysts for the partial hydrogenation of
20 block copolymers were disclosed, inter alia in US 3,700,748. In this document, the block copolymers were prepared by block polymerizing a monovinyl arene with butadiene, the butadiene block containing between about 8 and 80 % of 1,2-structure and thereafter were selectively hydrogenated so as to
25 substantially eliminate the unsaturation in the pendant vinyl groups. Hydrogenation was therein carried out in a solution of an inert hydrocarbon, preferably the same hydrocarbon solvent as employed during polymerization, and in the presence of certain catalysts, e.g. nickel acetyl acetonate reduced with
30 triethyl aluminum. According to this patent the catalyst predominantly hydrogenates all the pendant vinyl groups and not more than about 50 % of the unsaturation in the 1,4-structured portions of the block. Although the patent provides an example with partial hydrogenation (iodine number of 81

corresponding to 75 % conversion of the initial unsaturated olefinic carbon-carbon bonds) the selectivity has not been shown. When using nickel acetyl acetonate in a manner as described in the reference, the selectivity was found to be
5 insufficient. Rather, on repeating the experiment of said document using a polymer having a vinyl content of 45 % and using nickel acetyl acetonate at 1 ppm level, we found that at 75 % conversion of the carbon-carbon olefinic bonds, the 1,4-content was reduced to less than 30 %. When reducing the vinyl
10 content to 2 %, i.e. predominantly all of the 1,2-butadiene units, more than 60 % of the 1,4-butadiene recurring units were also hydrogenated. For polymers having initial vinyl content more than 45 %, longer times for hydrogenating the vinyl groups are required and as a result also more of the
15 1,4-olefinic bonds are hydrogenated. It is clear that the hydrogenation catalyst as illustrated in this document does not provide the desired selectivity, at least not for the whole range of polymers having a vinyl content of 8 to 80 %.

Generically, apart from nickel, also corresponding cobalt
20 and iron-containing catalysts were mentioned. However, this reference does not give any indication or suggestion that the corresponding cobalt or iron-containing catalysts would perform better in this respect. Indeed, using these catalysts at the same conditions as mentioned above would only have
25 confirmed the impression that the inventor of US 3,700,748 was too opportunistic. It was found that the same polymer hydrogenated in the presence of a cobalt catalyst reduced the 1,4-content in 1 hour to less than 10 %, whereas hydrogenation the same polymer in the presence of 1 ppm of an iron catalyst
30 did not show any significant activity at all.

This problem of poor selectivity was addressed and solved in WO 02/34799, disclosing methods for partially and selectively hydrogenating block polymers with other catalysts. For instance, a process for preparing a partially hydrogenated

butadiene polymer was described wherein a butadiene polymer comprising 1,2-butadiene recurring units and 1,4-butadiene recurring units was hydrogenated in the presence of hydrogen, using instead of the nickel catalyst of US 3,700,748, a
5 titanium-, zirconium-, and/or hafnium-based metallocene compound as hydrogenation catalyst and an alkali metal hydride co-catalyst. According to this method the 1,2-butadiene units were converted predominantly with hardly any conversion of the 1,4-butadiene units. A drawback of this method, however, is
10 the need of very expensive metallocene catalysts. Products made by this method are therefore inherently expensive.

It is therefore an object of the present invention to provide in a cheap catalyst that nevertheless gives excellent selectivity. Surprisingly, it was now found that despite the
15 teaching of US 3,700,748 iron-containing catalysts, at the right conditions, provide a much better selectivity than could be expected in view of the corresponding nickel catalysts.

Summary of the Invention

20 To this end the invention pertains to a method for partially and selectively hydrogenating a polymer made of at least a conjugated diene monomer having a vinyl content of from 20 to 65 %, comprising a hydrogenation step on a solution of the polymer, characterized in that the hydrogenation step
25 is performed in the presence of an iron-containing catalyst whereby a hydrogenated polymer is obtained wherein the vinyl content is reduced to 5 % or less, whereas the content of 1,4-olefinic bonds is maintained at a level of at least 30 %.

Products thus obtained can be used in many applications
30 wherein the color of the product does not play a role. However, for some applications the use of the thus obtained products is seriously hampered by the occurrence of strong rust colored stain of the product. It is therefore another objective of the present invention to provide a cheap catalyst

that has excellent selectivity properties on hydrogenating unsaturated block polymers with leaving as less as possible color thereon.

The invention therefore also pertains to methods that satisfy the above-mentioned objectives and that are moreover devoid of the disadvantages of the prior art methods, i.e. providing a cheap hydrogenation catalyst with excellent selectivity. To this end the invention further relates to a method for partially and selectively hydrogenating a polymer comprising a conjugated diene monomer wherein the hydrogenation step is performed by treating a solution of the polymer with an iron-containing catalyst and hydrogen to preferentially hydrogenate 1,2-double bonds over 1,4-double bonds, whereby the solution contains amounts of lithium alkoxide and iron-containing catalyst of which the ratio [lithium alkoxide]/[iron-containing catalyst] expressed as mole % is less than 20. The problem of rust color staining particularly occurs with low molecular weight polymers, for instance polymers having a molecular weight less than 20,000, making this method therefore particularly useful for such polymers.

Lithium alkoxide is commonly present in the reaction mixture as a result of the method for making polymers of conjugated dienes, which for instance comprises: a) anionically polymerizing conjugated diene monomers, optionally with other monomers, to produce polymers with living chain ends; b) terminating the living chain ends with an alcohol, to produce a terminated block copolymer and to give a polymer, such as for instance an SBS polymer, and a lithium alkoxide.

It was found that the method according to the invention leads to less colored or even uncolored products that are highly selectively hydrogenated. The term "highly selective" in this invention means selective hydrogenation of 1,2-olefinic bonds over 1,4-olefinic bonds whereby the ratio of

the percentage of the conversion of the 1,2-double bonds : the conversion of the 1,4-double bonds is at least 2 at a total conversion of 1,2-double and 1,4-double bonds of at least 40%. Preferably, this ratio is higher than 2.5.

5 It has been found important that the amount of lithium alkoxide in the product should be as low as possible, and preferably is not present at all. It was found that this aspect of the method is crucial for preventing the rust color stain of the end product. The amount of lithium alkoxide, such
10 as lithium methoxide or the lithium salt of 2-ethyl-1-hexanol, is expressed by its ratio to iron-containing catalyst that is present in the system. The ratio [lithium alkoxide]/[iron-containing catalyst] expressed as mole % should be less than 20, preferably less than 10, more preferably less than 5, and
15 most preferably about 0. Such low ratios, most preferably 0 (i.e. no lithium alkoxide at all), can preferably be obtained by using a different method of terminating the polymerization process. Such method was found by terminating the polymerization process by hydrogen, which leads to lithium
20 hydride rather than to lithium alkoxide. A combination of both termination methods (i.e. both alcohol and hydrogen termination) may also be used.

 It was further found that the rust color stain problem could also be solved in another manner, that is to say by
25 using a novel method of isolation of the product. According to this aspect the invention comprises a method wherein the hydrogenated polymer is extracted from the hydrogenating solution in the absence of an oxidation agent. Preferably, this extraction is performed in the absence of oxygen. A
30 further improvement in preventing staining of the product is to extract it from the hydrogenating solution with a solution of an organic acid having 8 to 36 carbon atoms, and in the absence of the oxidation agent.

Brief description of the Figure

The enclosed Figure 1 illustrates the improved selectivity of iron-containing catalysts versus nickel- or cobalt-containing catalyst.

5

Detailed description of the Invention

The iron-containing catalyst may be any iron-containing compound, such as a catalyst based on an iron salt including iron halide, iron carboxylate, iron acetyl acetonate, or iron alkoxide. A preferred catalyst is based on iron octanoate or iron 2-ethyl-1-hexanoate. The iron-containing catalyst for use in this invention can for instance be prepared by combining an iron carboxylate with a reducing agent, such as an alkyl aluminum, for instance in the manner as disclosed in US 5,057,582.

The catalyst is used in amounts of from 0.001 to 1, typically from 0.005 to 0.5 mmole per 100 g of unsaturated compound, and preferably in amounts in the range of from 0.01 to 0.1 mmole/100 g. Larger quantities of catalyst may be used to speed up the hydrogenation process, although this may increase the color stain. If possible also less catalyst may be used, to reduce the staining, costs, and environmental impact of the catalyst system.

The present invention further provides the hydrogenation reaction as a relatively straightforward and uncomplicated reaction. For instance, in a preferred embodiment a polymer solution containing living polymer is terminated by adding hydrogen under vigorous stirring until the typical color of living polymer has disappeared.

The catalysts of this invention can be used to hydrogenate the double bonds of any polymer made of conjugated diene monomers, such as butadiene and/or isoprene polymers, copolymers, and block copolymers. In particular, they may be used for the selective hydrogenation of a block polymer

comprising a polymer block of a vinyl aromatic monomer and a polymer block of a conjugated diene, such as butadiene and isoprene. The homopolymers, copolymers, and block copolymers are of medium molecular weight, i.e. having a weight average
5 molecular weight in the range from 500 to 1,000,000. More preferably, the method is used for low molecular weight polymers having molecular weights below 20,000.

Homo- and copolymers of particular interest are homo- and copolymers of 1,3-butadiene or isoprene, and optionally
10 another conjugated diene, and/or an aromatic vinyl compound such as styrene or alpha-methylstyrene and/or an acrylic compound, such as alkyl acrylate or alkyl methacrylate. Among these copolymers are included random copolymers in which the comonomers are randomly distributed along the polymer chain,
15 cross-linked copolymers, and pure or gradual block copolymers.

The block copolymers are especially interesting since some of them are thermoplastic elastomers, which are useful from an industrial point of view. Such block copolymer comprise (a) at least one polymer block predominantly made of
20 one or more aromatic vinyl compounds or predominantly made of one or more acrylic compounds, and (b) at least one polymer block predominantly made of a conjugated diene. The expression "predominantly" in this respect means for at least 80 mole %.

Other embodiments of block copolymers include linear,
25 branched, radial, and star copolymers. Another group of interesting block copolymers includes polymers comprising at least one polymer block predominantly made of butadiene, and at least one polymer block predominantly made of one or more conjugated diene monomers other than butadiene. The block
30 copolymers used preferably in this invention are the so-called styrenic block copolymers that contain between 10 to 90 wt.% of vinyl aromatic compounds. The preferred copolymers are those that contain approximately 20 to 65 wt.% of 1,2-vinyl bonds in the butadiene block.

The block copolymers may also be functionalized.

Derivatives may be obtained from block copolymers having at least one polymer block of an aromatic vinyl hydrocarbon and at least one polybutadiene block by hydrohalogenation, halogenation, carboxylation, epoxidation, hydroxylation, and chlorosulfonation. The polar derivatives so formed are useful for many commercial purposes.

The polymers made of conjugated diene monomers that can be hydrogenated according to this invention are usually obtained by a known anionic polymerization method. The anionic polymerization is especially interesting for producing polymers and copolymers that can be hydrogenated according to the invention. Among the initiators that can be used, the organo-lithium compounds are preferred, particularly butyl lithium compounds, such as n-butyl lithium and sec-butyl lithium.

Termination of the polymerization reaction is generally done by addition of a C₁-C₁₂ alcohol, such as a mono-alcohol or a polyol, an acid, including C₁-C₁₂ organic acids and mineral acids, a coupling agent such as an ester or silicon compound, water, or hydrogen, or by a combination of two or more of these methods. Examples of suitable alcohols are methanol and 2-ethyl-1-hexanol. It was found that addition of hydrogen rather than alcohol is strongly preferred because it leads to the formation of lithium hydride rather than to lithium alkoxide. It was found that the presence of a lithium alkoxide in a polymer solution has a strong negative impact on the stability of the iron-containing catalyst. In order to obtain the required 1,2-butadiene conversion levels, high amounts of iron-containing catalyst are necessary when substantial amounts of lithium alkoxide are present, and consequently the resulting polymers are strongly rust colored. The hydrogen termination method significantly adds to the success of the

present method, particularly when low molecular weight polymers are made.

Hydrogenation is preferably carried out in solution of an inert hydrocarbon, which preferably is the same hydrocarbon solvent as employed during polymerization. The term "inert solvent" means an organic solvent that does not react with any of the reactants that participate in the reaction. Examples of these inert solvents that are recommended are aliphatic hydrocarbons and cycloaliphatic hydrocarbons, such as n-hexane, n-octane, iso-octane, cyclohexane, methylcyclopentane, cyclopentane, ethers such as tetrahydrofuran, aromatic hydrocarbons such as benzene, toluene, and xylene, which are not hydrogenated under the selected reaction conditions, and mixtures of these solvents.

Conventional hydrogenation conditions may be applied. For instance, suitable hydrogen pressures are between 1 and 70 kg/cm², preferably between 5 and 50 kg/cm².

Suitable reaction temperatures vary from 20 to 150° C, preferably between 50 and 120° C. Ideally, the conditions are selected such as to approach near full conversion of the recurring vinyl or 1,2-butadiene units (i.e., less than 5 % vinyl groups) with substantially less conversion of the recurring 1,4-butadiene units (i.e., maintaining at least 30 % of the 1,4-butadiene recurring units). In respect of the preferred embodiment, starting with a polymer having a vinyl content in the range of 30 to 60 %, the condition are selected such as to hydrogenate the vinyl content to a degree of less than 3 %, whilst maintaining more than 30 % of the 1,4-butadiene recurring units.

The extraction method preferably used in the present invention comprises a treatment with an aqueous mineral acid, optionally in combination with an organic acid, and preferably without an oxidation step preceding the extraction step. It should be noted that the extraction of nickel-containing

catalysts with an organic acid is known from US patent No. 2,893,982. As an improvement in respect of this technology, in a further US patent No. 3,780,138 the combined use of an acid with an oxidation step has been propagated. Indeed, in more recent years use of dicarboxylic acids with oxygen or a similar oxidant have been mentioned, e.g., in US patent No. 4,595,749. In US patent No. 4,992,529 an extraction method is described wherein the solution of polymer with metals is contacted with an oxidizing agent, followed by treatment with a combination of mineral acid and organic acid. In view of this clear trend towards combined use of oxidation and acid extraction, it was now surprisingly found that in case of iron-containing catalyst the oxidation step should actually be avoided.

It is therefore preferred that the hydrogenated polymer is extracted from the hydrogenating solution in the absence of an oxidation agent, more specifically in the absence of oxygen. Extraction of the hydrogenating solution is preferably performed with a solution of an inorganic or organic acid, or a mixture thereof. Most preferably, the hydrogenated polymer is extracted from the hydrogenating solution with a solution of an organic acid having 8 to 36 carbon atoms.

The product resulting from this selective hydrogenation can be analyzed by ^1H -NMR spectroscopy to determine the presence or absence of vinyl groups. In the usual ^1H -NMR analysis, any 1,4-structure will show a chemical shift between 5.15 and 5.46 ppm. The 1,2-structure shows two shifts, namely between 4.75 and 5.10 ppm and between 5.46 and 5.73 ppm. It is desirable that in the final product substantially no signal is observed within the latter two chemical shift regions of the ^1H -NMR spectrum.

The hydrogenation products may be easily isolated from the solvent through known processes such as distillation, precipitation, chromatography, and the like.

The invention is illustrated by means of the following non-limitative examples.

Preparation of SBS block copolymers

5 Polymer A

A 30 l batch of polystyrene-polybutadiene-polystyrene (SBS) block copolymer having a molecular weight of 258,000 was prepared in a stainless steel reactor by sequential anionic polymerization using sec-butyl lithium as the initiator. The
10 polymerization was conducted in cyclohexane to which were added 150 ppm of diethoxypropane. At the end of the polymerization the living SBS-Li polymer was terminated with 1 equivalent of 2-ethyl-1-hexanol to produce a polymer solution comprising the polymer (SBS) and lithium 2-ethyl-1-hexanoxide.
15 The polymer solution contained 10.4 wt.% of polymer. The styrene content of the SBS polymer is 30 wt.% and the vinyl content of the mid-block is 40 mol.%.

Polymer B

Using the process as for Polymer A, a polymer solution
20 comprising a lower molecular weight Polymer B was made. The molecular weight was 110,000. The polymer solution contained 12.9 wt.% of Polymer B.

Polymer C

In a similar manner as for Polymer B, except using
25 hydrogen instead of 2-ethyl-1-hexanol for terminating the polymerization, a hydrogen-terminated Polymer C was made.

At the end of the polymerization reaction the reactor was sparged with hydrogen to terminate the living SBS-Li polymer and to produce a polymer solution comprising Polymer C (SBS)
30 and LiH.

Catalyst preparation

Catalysts were prepared as solutions having a Ni (comparison examples) or Fe concentration of 1000-1500 ppm

(parts per million). The catalysts were prepared using nickel octanoate or iron 2-ethyl-1-hexanoate by diluting the Ni, Co, or Fe carboxylates in cyclohexane and then slowly adding triethyl aluminum to obtain a 3.0/1 molar ratio of Al/M
5 (wherein M = Ni, Co, or Fe).

Hydrogenation of SBS block copolymer

A stainless steel reactor was charged with 800 g of SBS polymer solution, prepared as described above. The temperature
10 of the reactor was kept constant. A catalyst suspension of nickel-, cobalt-, or iron-containing catalyst was added to the reactor and the hydrogen pressure was raised to 40 bar. Immediately, an exothermic reaction started. The hydrogenation was allowed to run for several hours, during which period
15 samples were drawn from the reactor and analyzed by ^1H -NMR to determine the conversion of the olefinic double bonds.

Example 1 and 2 (comparison)

An SBS polymer solution of Polymer A was hydrogenated
20 using 1 ppm of Ni or Co catalyst in the polymer solution. The temperature of the reactor was kept constant at 40° C. The results are given in Table 1.

Example 3

25 An SBS polymer solution of Polymer A was hydrogenated using 5 ppm of Fe catalyst in the polymer solution. The temperature of the reactor was kept constant at 70° C. The lithium alkoxide/Fe-containing catalyst molar ratio 6.7 is given with molar ratios of other examples in Table 3. The
30 results are given in Table 1.

Comparison Example 1 and 2 shows that the method according to US 3,700,748 did not give acceptable selectivity of reduction of 1,2-butadiene recurring units over 1,4-butadiene recurring units.

Table 1: Conversion data of hydrogenation experiments with Ni and Fe catalyst

Comparison Example 1 1 ppm Ni				Comparison Example 2 1 ppm Co				Example 3 5 ppm Fe			
time (min)	1,2 C=C con- tent (%)	1,4 C=C con- tent (%)	1,4 C=C conv. (%)	time (min)	1,2 C=C con- tent (%)	1,4 C=C con- tent (%)	1,4 C=C conv (%)	time (min)	1,2 C=C con- tent (%)	1,4 C=C con- tent (%)	1,4 C=C conv (%)
0	45.0	53.4	0.0	0	45.0	53.4	0.0	0	45.0	53.4	0.0
5	37.2	49.8	6.6	10	23.3	42.1	21.1	5	11.2	42.8	19.9
10	29.6	46.7	12.6	20	10.2	30.9	42.1	10	5.6	41.2	22.8
20	19.9	39.8	25.4	35	2.6	17.3	67.5	25	2.9	35.3	33.9
35	10.6	34.2	35.9	60	0.4	7.5	85.9	50	1.2	29.0	45.7
60	4.6	27.3	48.9					90	0.0	24.9	53.3
100	2.1	21.3	60.1								
160	1.0	17.2	67.8								

5 Example 4

An SBS polymer solution of Polymer B was hydrogenated using 5 ppm of Fe catalyst in the polymer solution. The temperature of the reactor was kept constant at 60° C. The results are given in Table 2.

10 Example 5

The reactor was charged with Polymer C. 2-ethyl-1-hexanol was added to convert 66 % of the LiH to the lithium alkoxide. The hydrogenation was carried out as in Example 3. The results are given in Table 2.

15 Example 6

The reactor was charged with Polymer C. 2-ethyl-1-hexanol was added to convert 45 % of the LiH to the lithium alkoxide.

The hydrogenation was carried out as in Example 3. The results are given in Table 2.

Example 7

- 5 The reactor was charged with Polymer C. The hydrogenation was carried out as in Example 3. The results are given in Table 2.

Example 8

- 10 The reactor was charged with Polymer C. The SBS polymer solution was hydrogenated using 1 ppm of Fe catalyst in the polymer solution. The temperature of the reactor was kept constant at 60° C. The results are given in Table 2.

- 15 Table 2: Conversion data for polymer solutions with various lithium alkoxide amounts

	Example 4		Example 5		Example 6		Example 7		Example 8	
	1 eq of 2-EH*		0.66 eq of 2-EH		0.45 eq of 2-EH		no 2-EH		no 2-EH 1 ppm Fe	
Time (min)	1,2 C=C (%)	1,4 C=C (%)	1,2 C=C (%)	1,4 C=C (%)	1,2 C=C (%)	1,4 C=C (%)	1,2 C=C (%)	1,4 C=C (%)	1,2 C=C (%)	1,4 C=C (%)
0	45.0	55.0	45.0	55.0	45.0	55.0	45.0	55.0	45.0	55.0
5							9.1	46.2		
15							0	28		
70			2.8	40.6	1.9	37.2				
120			2	38.1	1	32.4			6.6	46.2
200	9.5	49.3	1.2	35.7	0.6	28.4			3.6	41.5

* 2-EH stand for 2-ethyl-1-hexanol

- 20 In Table 3 the molecular ratio of the lithium salt of 2-ethyl-1-hexanol and iron-containing catalyst for Examples 4 to 7 and the activity of the iron-containing catalyst in these polymer solutions are given. The amount of staining was

determined indirectly by measuring the ratio at the same amount of staining. Higher ratio's mean that the hydrogenation conversion is insufficient or that the reaction does not come to an end.

5

Table 3: Molar ratio of lithium alkoxide and iron and catalyst stability

Example	[Li alkoxide]/[Fe catalyst] (mole/mole)	Catalyst activity*
4	21.4	Poor
5	14	Acceptable
6	9.6	Good
7	0	Very good
8	0	Very good

* >90 % conversion of 1,2-olefinic bonds for 5 ppm of catalyst at 60° C within:

- 10 30 min (very good);
1 h (good);
4 h (acceptable);
more than 4 h (poor).

15 Metal extraction

Polymer D

Polymer D is a branched SBS type polymer having a styrene content of about 25 % wt, a mole weight of 315,000, a vinyl content of about 60 %, a couplings efficiency of about 67 % (using diethyl adipate as a couplings agent). The polymer solution contained about 9 wt.% of polymer in cyclohexane. The polymer was partially selectively hydrogenated using 20 ppm of Fe catalyst in the polymer solution. After hydrogenation the vinyl content of the polymer is about 5 % and the 1,4-double bonds content 29 %. The polymer solution was maintained under a nitrogen blanket after hydrogenation.

Example 9

The extractions were performed in a 3 liter glass vessel at 75° C, which was thoroughly purged with nitrogen. To the vessel was added 0.8 liter of acid (0.5 wt.% H₂SO₄ in water).
5 Nitrogen was bubbled through the solution for 30 minutes to suppress oxygen. 0.8 kg of the polymer solution D was added to the vessel under vigorous mixing (1200 rpm). Air was bubbled through the mixture for one minute. The pressure during extraction was maintained at less than 0.2 MPa. After 60
10 minutes the mixer was stopped and the contents were allowed to phase separate for 20 minutes. The aqueous phase was fully drained from the extraction vessel. A polymer solution sample was then taken. The sample was centrifuged in order to remove water. The amount of iron in the polymer was determined by
15 inductively coupled plasma/mass spectroscopy (ICP/MS). The results are given in Table 4.

Example 10

Example 9 was repeated. However, in this experiment no
20 air was bubbled through the mixture of dilute acid and polymer solution. Again, the results are given in Table 4.

Example 11

To the polymer solution of Example 9 was added 400 ppm of
25 neodecanoic acid. Metals were removed according to the process as described above. The results are given in Table 4.

Example 12

Similar to Example 10, to the polymer solution was added
30 400 ppm of neodecanoic acid. In this experiment no air was bubbled through the mixture of dilute acid and polymer solution. The results are given in Table 4.

Table 4: Iron content of polymers after metal extraction under various conditions

Example	O ₂ purge	Inorganic acid	Organic acid	Fe prior to wash (ppm)	Fe after wash (ppm)
9	yes	yes	-	219	121
10	no	yes	-	219	41
11	yes	yes	400 ppm NDA*	219	6
12	no	yes	400 ppm NDA	219	<5**

(*) NDA is neodecanoic acid

(**) Detection limit is 5 ppm of metal on polymer

Claims:

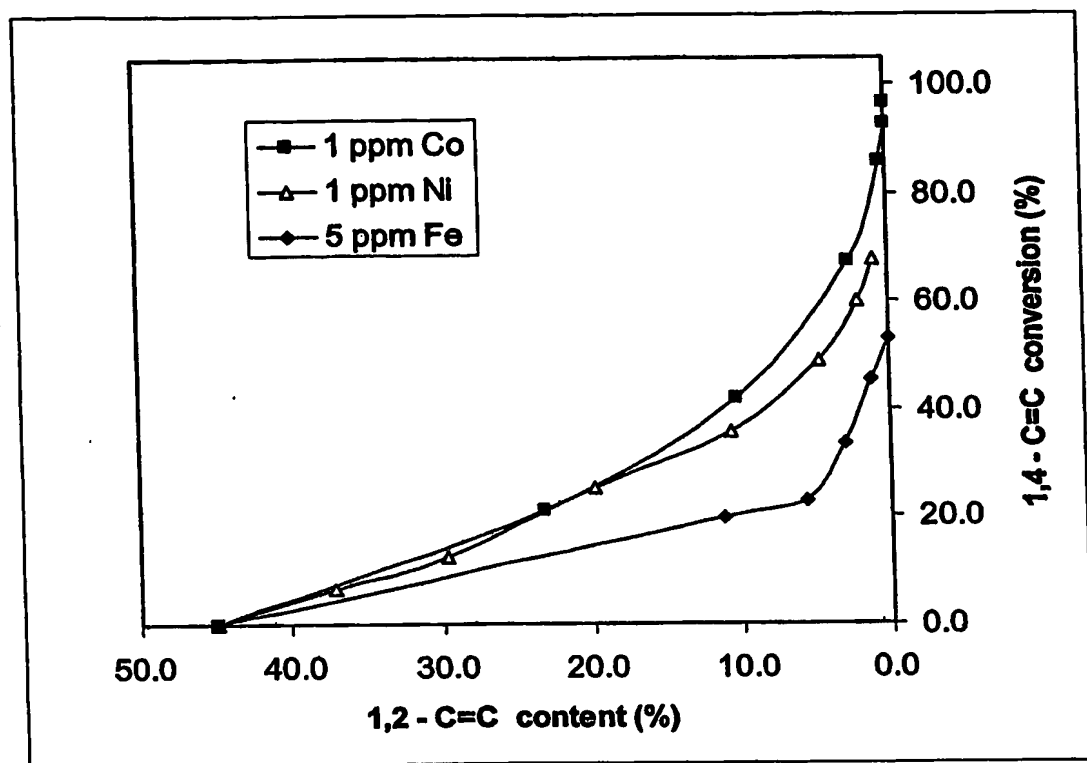
1. A method for partially and selectively hydrogenating a polymer made of at least a conjugated diene monomer having a vinyl content of from 20 to 65 %, comprising a hydrogenation step on a solution of the polymer, characterized in that the hydrogenation step is performed in the presence of an iron-containing catalyst whereby a hydrogenated polymer is obtained wherein the vinyl content is reduced to 5 % or less, whereas the content of 1,4-olefinic bonds is maintained at a level of at least 30 %.
2. The method according to claim 1 for partially and selectively hydrogenating a polymer made of at least a conjugated diene monomer having a vinyl content of from 30 to 60 %, wherein the hydrogenated polymer is obtained wherein the vinyl content is reduced to 3 % or less, whereas the content of 1,4-olefinic bonds is maintained at a level of at least 30 %.
3. The method according to claim 1 or 2 wherein the polymer is a block polymer comprising at least a polymer block of a vinyl aromatic monomer and a polymer block of a conjugated diene monomer.
4. The method according to any one of claim 1-3 wherein the solution that is subjected to the hydrogenation step contains amounts of lithium alkoxide and iron-containing catalyst of which the ratio [lithium alkoxide]/[iron-containing catalyst] expressed as mole % is less than 20.
5. The method according to any one of claims 1-4 wherein the polymer is a substantially completely hydrogen terminated polymer.
6. The method according to any one of claims 1-5 wherein the solution is substantially free from lithium alkoxide.

7. The method according to any one of claims 1-6 wherein the hydrogenated polymer is extracted from the hydrogenating solution in the absence of an oxidation agent.
8. The method according to claim 7 wherein the hydrogenated
5 polymer is extracted in the absence of oxygen.
9. The method according to claim 7 or 8 wherein the hydrogenated polymer is extracted from the hydrogenating solution with a solution of an inorganic or organic acid, or a mixture thereof.
- 10 10. The method according to claim 9 wherein the hydrogenated polymer is extracted from the hydrogenating solution with a solution of an organic acid having 8 to 36 carbon atoms.

Abstract:

The invention relates to a method for partially and selectively hydrogenating a polymer made of at least a conjugated diene monomer having a vinyl content of from 20 to 65 %, comprising a hydrogenation step on a solution of the
5 polymer, characterized in that the hydrogenation step is performed in the presence of an iron-containing catalyst whereby a hydrogenated polymer is obtained wherein the vinyl content is reduced to 5 % or less, whereas the content of 1,4-olefinic bonds is maintained at a level of at least 30 %.

Figure 1



PROT/EP2004/051439



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:



BLACK BORDERS



IMAGE CUT OFF AT TOP, BOTTOM OR SIDES



FADED TEXT OR DRAWING



BLURRED OR ILLEGIBLE TEXT OR DRAWING



SKEWED/SLANTED IMAGES



COLOR OR BLACK AND WHITE PHOTOGRAPHS



GRAY SCALE DOCUMENTS



LINES OR MARKS ON ORIGINAL DOCUMENT



REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY



OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.